

SEMI-ANALYTICAL SOLUTIONS FOR THE TRANSPORT OF REACTIVE SOLUTE IN HOMOGENEOUS POROUS MEDIA

by

Kunchala Rama Manohar



DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

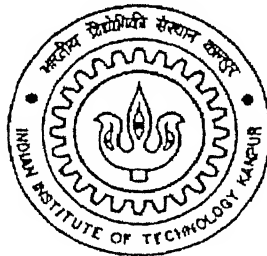
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SEMI-ANALYTICAL SOLUTIONS FOR THE TRANSPORT OF REACTIVE SOLUTE IN HOMOGENEOUS POROUS MEDIA

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

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Submitted by
Kunchala Rama Manohar

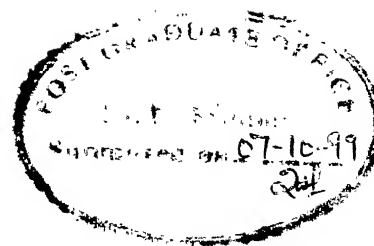


Department of Civil Engineering
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CERTIFICATE



This is to certify that this is a bonafied thesis work entitled “**Semi-analytical solutions for the transport of reactive solute in homogeneous porous media**”, by Mr. Kunchala Rama Manohar, in partial fulfillment of the requirements for the degree of Master of Technology in Civil Engineering of Indian Institute of Technology Kanpur. It has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

A handwritten signature in black ink, reading "Rajesh Srivastava".

Dr. Rajesh Srivastava
Associate Professor
Department of Civil Engineering
Indian Institute of Technology Kanpur
Kanpur – 208 016, INDIA.

October
IIT Kanpur

MADAM

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ABSTRACT

The transport of chemically reactive solutes through porous media is generally affected by multiple reactions with different rate constants. In this study, transport phenomena affected by rate limited sorption, first-order mass transfer and first-order transformation is studied. The governing equations are taken in their most general form for the analysis. Analytical solutions are developed using the laplace transform approach.

Exact solutions for batch reactor problems are arrived at. Semi-analytical solutions are developed for lab scale transport systems with constant hydrodynamic dispersion coefficient. Analytical expressions are developed for temporal moments of the plume. An effective numerical technique to invert the laplace transform is used to obtain the break-through curves. The temporal behavior of the phenomenon under different rate-constant values is studied. The results from the present study are compared with the field experiments and they are found matching closely.

These solutions will help in determine a criterion for the permissible time step length for a good numerical solution of the transport problem and to test the accuracy of the simulation codes. They will also be useful as a preliminary analysis tools for ascertaining the relative importance of various processes for given conditions.

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NOTATIONS

a	:	Input parameter in inversion technique
C_a	:	Concentration of solute in advective region
C_n	:	Concentration of solute in nonadvective region
C_0	:	Reference concentration
C_{a0}	:	Initial concentration of solid phase solute in advective region
C_{n0}	:	Initial concentration of solid phase solute in nonadvective region
D	:	Hydrodynamic dispersion coefficient
D_{eff}^t	:	Effective dispersion coefficient
f	:	Mass fraction of the sorbent in the advective region
F	:	Fraction of sorbent with instantaneous sorption
$G(p)$:	The function of the laplace variable with a ratio of polynomials
$H(p)$:	$1/G(p)$
$H(0)$:	$H(p) \big _{p=0}$
K	:	Equilibrium sorption coefficient
k_{a2}	:	First order reverse sorption rate-constant in advective region
k_{n2}	:	First order reverse sorption rate-constant in nonadvective region
l	:	Input parameter in the inversion technique
m	:	Input parameter in the inversion technique
M_n^t	:	n^{th} absolute temporal moment of the concentration
p	:	Laplace variable
q	:	Specific discharge
S_{a2}	:	Rate-limited sorbed phase concentration in advective region

S_{a0}	:	Initial concentration of the sorbed phase solute in advective region
S_{n2}	:	Rate-limited sorbed phase concentration in nonadvective region
S_{n0}	:	Initial concentration of sorbed phase solute in nonadvective region
t	:	Time
t_0	:	Pulse duration
T	:	Reference time
v_{eff}^t	:	Effective velocity
x	:	Distance
θ_a	:	Fractional volumetric water content of advective region
θ_n	:	Fractional volumetric water content of nonadvective region
ρ	:	Bulk density of the porous medium
α	:	First order mass transfer coefficient
μ_{a1}	:	Transformation coefficient for instantaneous sorption
μ_{a2}	:	Transformation coefficient for rate-limited sorption
μ_n^t	:	n^{th} absolute moment of C_a normalized with mass

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Chapter 1

INTRODUCTION

1.1 General Introduction

The quality of water is of major interest in any development and management of water resources system. With the increased demand for water in most parts of the world, and with the intensification of water utilization, the quality problem becomes the limiting factor in the development of water resources. The quality of both surface and groundwater resources is deteriorating as a result of pollution. Special attention should be devoted to the pollution of ground water due to their very slow velocities. Although it seems that groundwater is more protected than surface water against pollution, it is still subject to pollution, and when the contamination of groundwater occurs, the restoration to the original, non-polluted state is more difficult. Due to the potential of the problem, the accuracy in the estimation of the extent of pollution assumes great importance. In technical terms, this problem of groundwater pollution is treated as mass transport phenomenon in porous media, where the considered mass is that of some

solute or pollutant moving with the solvent which is water in the interstices of the porous medium.

The principle mechanisms affecting the transport of a solute in a porous medium are convection, mechanical dispersion, molecular diffusion, solid-solute interactions and various chemical reactions and decay phenomena, which may be regarded as source-sink phenomena for the solute.

For mass transport phenomena, mathematical analysis and quantification starts at mass conservation equation which states that the difference between mass inflow rate and mass outflow rate should be equal to the change in mass storage with time. For systems, which involve processes like advection, diffusion, dispersion and etc, and if the tracer is ideal, this expression suffices.

But when the phenomenon involves a chemically reactive element in the mass that is being transported, the mass conservation equation should be expanded so as to incorporate this also. The material, while getting transported, may disintegrate or the porous medium, depending on its composition, may contribute to the mass. The mass conservation equations gets modified in terms of source or sink terms, depending on whether a constituent is being added to the mass or removed by chemical processes. Then the appropriate statement for mass conservation when reactions are considered would be,

Mass inflow rate – Mass outflow rate \pm Mass production rate = Change of mass with time.

The plus or minus sign designates either a source or a sink and takes on different forms for different reactions. For convenience, the source or sink terms are quantified as mass, produced or consumed per unit volume per unit time. Transport involving several dissolved species in the transport requires a system of mass conservation equations, one for each constituent. Appropriate rate laws are used to express the reactions mathematically, depending on the reaction.

Reactions are classified as homogeneous, operating within a single phase, or heterogeneous, operating between two phases, such as, solid and liquid. Also, reactions can be described from an equilibrium or kinetic point of view depending on the rate of the reaction relative to the mass transport process.

1.2 Review of Literature

The transport of chemically and biologically reactive solute through porous media, is affected by various rate-limited processes (Brusseau, 1989). Several techniques have been reported in the literature for numerical simulation of the advective-dispersive-reactive (ADR) equation in the presence of rate-limited processes. These include the modified method of characteristics and mixed finite elements method (Chiang et al 1989), split-operator, Petrov-Galerkin methods (Miller, 1993). Fry [1993] reported an analytical solution to the solute transport equation with rate-limited desorption and decay. Tompson [1993] gave a numerical simulation technique for chemical migration in physically and chemically heterogeneous porous media. Daus et al [1985], tested various finite element formulations of the advection-dispersion equation and gave a comparative error analysis among those models. Relative errors are tabulated for various different models. An analytical solution for describing the transport phenomena in heterogeneous media with a distance dependent dispersion relation has been developed by Yates [1990]. He, first transformed the advection-dispersion equation with space-dependent dispersion coefficient, in to laplace domain, and then used contour integration techniques to invert in to original time domain. Goltz et al [1986], solved the three dimensional solute transport problem in infinite medium with mobile and immobile zones. Brusseau et al [1992], discussed the difficulties and factors to be considered while modeling transport phenomenon influenced by multi-process nonequilibrium and transformation reactions. Valocchi [1992], discussed the accuracy of operator splitting techniques of ADR problems.

The formulation suggested by Brusseau [1991] is quite general and includes various other models as its special cases. It is therefore used as the basis for the present study.

1.3 Objective of the present study

With the advent of high speed computing facilities, numerical methods are gaining more popularity for modeling reactive chemical migration through porous media. In such cases, evaluating the effect of multiple reactions on the time discretization becomes critical. The objective of the present study is to provide a basis to address that problem, by developing analytical and semi-analytical solutions for one-dimensional transport of reactive contaminants through porous media undergoing rate-limited sorption and first order mass transfer and transformation at a generic level. Laplace transform is used to solve the equations. The batch reactor systems or point-process systems and laboratory scale column transport systems are to be solved analytically, at a generic level. Expressions are to be developed to obtain the quantities of practical significance and from them, the temporal dependency of the phenomenon is to be studied. The analytical solutions are to be tested by using numerical techniques to invert the equations in laplace domain in to original time domain. The effect of the rate constants on the transport phenomenon is to be studied. The results from the study are to be compared with the experimental data available in the literature.

Chapter 2

MODEL

2.1 Introduction

Theories on dispersion, so far published, suggest two approaches to model mass transport phenomenon in porous medium. The main effort has been to express hydrodynamic dispersion macroscopically through a partial differential equation and to determine the nature of coefficients, which appear in this equation. Literature suggests two broad ways to model this problem. In one approach, the porous medium is replaced by a fictitious, greatly simplified, model in which the spreading of a solute can be analyzed by exact mathematical methods. Single capillary tubes, a bundle of capillaries, an array of mixing cells, are examples of such models. The second approach is to construct a conceptual statistical model of the microscopic motion of solute particles and to average these motions in order to obtain a macroscopic description of them.

Many types of models used to describe the transport of solutes in porous media are based on the convection-dispersion equation as given by Bear [1972, 1979]. The convection-dispersion equation may include terms, which describe the hydrodynamic

dispersion, fluid advection, linear equilibrium, first-order reaction and possibly zeroth order production. Models describing the chemical reactivity of the contaminant and the phase, in which it occurs, also use the same model.

The reactions can be categorized as biodegradation, radioactive decay, hydrolysis etc. In general, models make assumptions about the phase of the contaminant, whether the contaminant exists in solid phase or liquid phase or both. The mixing is assumed to occur in various domains, such as advective, nonadvective. The complexity of the model is influenced by the occurrence of mass transformation and rate limited sorption in various phases. Allowing these reactions makes the model more complex.

2.2 Model Description

For the present study, a two-phase, two-domain contaminant transport model has been assumed. Apart from mechanical mixing and microdispersion, the transport is influenced by reactivity of the solute. In this model, the entire flow domain is assumed to be divided into two regions namely, 1) Advective Region 2) Nonadvective region. The mass balance equation is applied on both regions separately. At the grain level, the mixing is influenced by the sorption on the surface of the particle. Every particle in the flow domain consists of two sites on surface namely equilibrium site and rate limited site. The contaminant is assumed to be chemically reactive and to be existing in both solution phase and solid phase. The rate-limited sorption is used to represent chemical reaction and diffusional processes and the first-order mass transfer is used to represent the macro-scale heterogeneity by mass transfer between advective and non-advective regions of any size, shape or type. The transformation coefficients are used to represent irreversible transformation reactions at a generic level. First order transformation accurately describes the radioactive decay. Biodegradation is usually specified to occur in the solution phase but radioactive decay and hydrolysis reactions may occur in any phase. That means, transformation is allowed to occur in any phase and any domain.

2.3 Governing Equations

The governing equation for the transport of a reactive chemical through the advective region of a porous medium is given by (Brusseu, 1991)

$$\begin{aligned} (\theta_a + f \rho F_a K_a) \frac{\partial C_a^*}{\partial t^*} + f \rho \frac{\partial S_{a2}^*}{\partial t^*} = \frac{\partial}{\partial x_i^*} \left(\theta_a D_{ij}^* \frac{\partial C_a^*}{\partial x_j^*} \right) - q_i^* \frac{\partial C_a^*}{\partial x_i^*} \quad (2.1) \\ - \alpha^* (C_a^* - C_n^*) - (\mu_a^* \theta_a + \mu_{a1}^* f \rho F_a K_a) C_a^* - \mu_{a2}^* f \rho S_{a2}^* \end{aligned}$$

Where,

θ_a is fractional volumetric water content of the advective region (L^0),

f is mass fraction of the sorbent constituting the advective region (M^0),

ρ is the bulk density of the porous medium (ML^{-3}),

F is the fraction of the sorbent with instantaneous sorption,

K is the equilibrium sorption coefficient (L^3M^{-1}),

C is the concentration of the solute in solution (ML^{-3}),

t is the time (T),

S_2 is the rate-limited sorbed-phase concentration ($M M^{-1}$),

x_i is the coordinate directions (L),

D_{ij} is the hydrodynamic dispersion tensor (L^2T^{-1}),

q_i are the specific discharge components (LT^{-1}),

α is the first order coefficient for mass transfer between the advective and nonadvective regions (T^{-1}),

μ_1 and μ_2 are the transformation coefficients (T^{-1}) for the instantaneous and rate-limited sorbed-phase domains, respectively.

Subscript a , refers to the advective region. Similar parameters in the nonadvective domain are denoted with the subscript n , and the superscript $*$ is used to

distinguish the notations for these variables from their nondimensional counterparts which will come in the later sections.

The mass balance of the nonadvective domain can be described by the following equation.

$$\begin{aligned} (\theta_n + (1-f) \rho F_n K_n) \frac{\partial C_n^*}{\partial t^*} + (1-f) \rho \frac{\partial S_{n2}^*}{\partial t^*} = & \alpha^* (C_a^* - C_n^*) \\ - (\mu_n^* \theta_n + \mu_{n1}^* (1-f) \rho F_n K_n) C_n^* + \mu_{n2}^* (1-f) \rho S_{n2}^* \end{aligned} \quad (2.2)$$

Dynamics of sorption and transformation for the rate-limited domains are described by the following equations.

$$\frac{\partial S_{n2}^*}{\partial t^*} = k_{n2}^* [(1-F_n) K_n C_n^* - S_{n2}^*] - \mu_{n2}^* S_{n2}^* \quad (2.3)$$

$$\frac{\partial S_{a2}^*}{\partial t^*} = k_{a2}^* [(1-F_a) K_a C_a^* - S_{a2}^*] - \mu_{a2}^* S_{a2}^* \quad (2.4)$$

Where, k_{a2}^* and k_{n2}^* are the first-order reverse sorption rate coefficients (T^{-1}) for the advective and nonadvective regions, respectively.

The laplace transform can be applied on a function so as to make the behavior of the function smoother than in the original domain. Let $f(t)$ is a real valued

function defined over the interval $(-\alpha, \alpha)$ such that $f(t) = 0$ for all $t < 0$. The laplace transform of $f(t)$, denoted by $L\{f(t)\}$ is defined as,

$$L\{f(t)\} = F(s) = \int_0^{\infty} f(t) e^{-st} ds \quad (2.5)$$

Where, parameter s is called laplace variable, independent of space and time and can be real or complex number. The laplace transform of $f(t)$ is said to exist if the integral (2.5) is convergent for some value of s .

Chapter 3

MATHEMATICAL ANALYSIS

3.1 Introduction

This chapter describes the mathematical analysis done to solve ADR equation analytically. The governing equations are expressed according to the assumptions made regarding the solute and medium. Then the equations are nondimensionalized using appropriate nondimensional parameters. The equations in the nondimensional form are transformed in to the laplace domain using the definition of laplace transform, given in section 2.3.

3.2 Assumptions made about the solute and medium

In order to solve the one-dimensional classic ADR equation analytically, certain assumptions are made regarding the phenomenon of solute transport in porous medium. They are,

- 1) The medium is homogenous and isotropic.
- 2) The phenomenon is one-dimensional.

- 3) The medium is fully saturated.
- 4) Transformation coefficients are used to represent irreversible reactions.

3.3 Non-Dimensionalization

The governing equations are non-dimensionalized so as to get the equations in a form free from the units of the parameters being used for calculations. The equations are made more tractable to solve analytically, by doing so. The non-dimensional parameters are defined for advective domain and non-advective domain similarly. For advective domain, they are given in table 3.1.

Table 3.1 Nondimensional parameters for advective region

Parameter	Definition
C_a	C_a^*/C_0
S_a	$S_{a2}^*/(1-F_a) K_a C_0$
t	t^*/T
D	$\theta_a D^* \theta R_{a1}/q^{*2} T$
x	$x^* \theta R_{a1}/q^* T$
R_{a1}	$\phi_a + f \rho (1-F_a) K_a / \theta$
R_{a2}	$f \rho F_a K_a / \theta$
ω	$\alpha^* T / \theta$
ξ_{a1}	$(\mu_a^* \phi_a + \mu_{a1}^* f \rho F_a K_a / \theta) T$
ξ_{a2}	$R_{a2} \mu_{a2}^* T$
k_{a2}	$k_{a2}^* T$
v_a	$k_{a2} + \mu_{a2}^* T$
γ_{a1}	$R_{a1} v_a + \xi_{a1} + R_{a2} k_{a2}$
γ_{a2}^2	$v_a \xi_{a1} + k_{a2} \xi_{a1}$

Where, $\theta = \theta_a + \theta_n$

$$\phi_a = \theta_a/\theta$$

$$S_{a1} = K_a C_a$$

$$S_{n1} = K_n C_n$$

S_{a1} and S_{n1} are the concentrations of solid phase solute in the equilibrium sites of advective and nonadvective regions, respectively. Similar nondimensional parameters are defined for the nonadvective domain variables also. They are given in table 3.2.

Table 3.2 Nondimensional parameters for nonadvective region

Parameter	Definition
C_n	C_n^*/C_0
S_n	$S_{n2}^*/(1-F_n) K_n C_0$
R_{n1}	$\phi_n + (1-f)\rho(1-F_n)K_n/\theta$
R_{n2}	$(1-f)\rho(1-F_n)K_n/\theta$
ξ_{n1}	$(\mu_n^* \phi_n + \mu_{n1}^* (1-f)\rho F_n K_n/\theta) T$
ξ_{n2}	$R_{n2} \mu_{n2}^* T$
k_{n2}	$k_{n2}^* T$
v_n	$k_{n2} + \mu_{n2}^* T$
γ_{n1}	$R_{n1} v_n + \xi_{n1} + R_{n2} k_{n2}$
γ_{n2}^2	$v_n \xi_{n1} + k_{n2} \xi_{n1}$

Where, $\phi_n = \theta_n/\theta$

The above-defined nondimensional parameters are substituted in the equations, (2.1), (2.2), (2.3) and (2.4) and are simplified. It is assumed that the volumetric

water content and the dispersion coefficient are spatially invariable. Also for notational convenience, it is assumed that neither R_{a1} nor R_{n1} are zero. If R_{n1} is zero, all the parameters in the nonadvective domain can be set to zero. The mass balance equations for advective and nonadvective domain takes the form as given below, respectively.

$$R_{a1} \frac{\partial C_a}{\partial t} + R_{a2} \frac{\partial S_a}{\partial t} = R_{a1} D \frac{\partial^2 C_a}{\partial x^2} - R_{a1} \frac{\partial C_a}{\partial x} - \omega_a (C_a - C_n) - \xi_{a1} C_a - \xi_{a2} S_a \quad (3.1)$$

$$R_{n1} \frac{\partial C_n}{\partial t} + R_{n2} \frac{\partial S_n}{\partial t} = \omega_n (C_a - C_n) - \xi_{n1} C_n - \xi_{n2} S_n \quad (3.2)$$

The governing equations for the dynamics of rate limited sorption for both advective and nonadvective domain are also nondimensionalized. They take the form given below. For the rate-limited sorption in advective domain,

$$\frac{\partial S_a}{\partial t} = k_{a2} C_a - v_a S_a \quad (3.3)$$

The governing equation for rate-limited sorption in nonadvective domain, after nondimensionalization,

$$\frac{\partial S_a}{\partial t} = k_{a2} C_a - v_a S_a \quad (3.4)$$

The equations, (3.1) and (3.2) together with the sorption dynamics equations, (3.3) and (3.4) can be solved to obtain the non-dimensional concentrations C_a , C_n , S_{a2} and S_{n2} for given initial and boundary conditions.

3.4 Transforming into laplace domain

The equations given in the previous section involve partial derivatives and solving it analytically, in real domain needs many assumptions. To solve them in their existing form, they are transformed into laplace domain using the definition given in (2.5). The laplace transform is used to eliminate time dependency in the equations. In laplace domain, solutions are generally smoother than in the time domain. In addition, the solutions for different times are independent (or parallel), in the sense that, solution for one time is not dependent on solution for some other time, which means that the problem of numerical error accumulation is not encountered.

Taking the laplace transform of the equations (3.2)-(3.4), and assuming that the initial mass of solute can exist in any phase and any domain, yields the following expressions. The rate-limited sorption equations become,

$$\bar{S}_a = \frac{k_{a2}\bar{C}_a + S_{a0}}{p + v_a} \quad (3.5)$$

$$\bar{S}_n = \frac{k_{n2}\bar{C}_n + S_{n0}}{p + v_n} \quad (3.6)$$

The mass balance equation for nonadvective domain becomes,

$$\bar{C}_n = \frac{\omega}{\gamma_n + \omega} \bar{C}_{a0} + \frac{R_{n1}}{\gamma_n + \omega} C_{n0} + \frac{S_{n0}}{\gamma_n + \omega} \left\{ \frac{R_{n2} k_{n2}}{p + v_n} \right\} \quad (3.7)$$

In which,

$$\gamma_n = \frac{R_{n1}p^2 + \gamma_{n1}p + \gamma_{n2}^2}{p + v_n} \quad (3.8)$$

Where, p is the laplace variable, which is independent of space and time and can be real or complex. The overbar indicates the concentration equivalents in laplace domain. S_{a0} is the initial concentration of solute in solid phase and in advective domain, S_{n0} , in solid phase and in nonadvective domain, and C_{a0} is the concentration of solute in advective domain, liquid phase. The subscript a, denotes advective domain and n, nonadvective domain. In order to get the laplace equivalent of C_a , the equation (3.1) would be transformed in to laplace domain depending on the assumed conditions about the phenomena. They will be described in the next chapter.

Chapter 4

SOLUTIONS

4.1 Introduction

This chapter describes the solutions for two different transport systems namely batch reactor system and column transport system. Laplace transform is applied on equation (3.1) for both the cases separately, depending on the assumptions made. Then they are inverted from laplace domain to original time domain, in order to obtain the nondimensional concentrations.

4.2 Batch Reactor System

For batch reactor problems, the phenomenon is assumed to be local. That means the process is essentially treated as point process. The concentration is considered to be spatially invariable. With this assumption, the spatial terms in the equation (3.1) will become zero. Also, for point processes, the reference time T is taken as one unit.

Applying laplace transform on (3.1) with the above assumptions and substituting (3.2), (3.2) and (3.4) results in the following expression.

$$\left[\gamma_a + \omega \frac{\gamma_n}{\gamma_n + \omega} \right] \bar{C}_a = R_{a1} C_{a0} + \frac{\omega R_{n1}}{\gamma_n + \omega} C_{n0} + \frac{R_{a2} k_{a2}}{p + \nu_a} S_{a0} + \left[\frac{\omega}{\gamma_n + \omega} \right] \left[\frac{R_{n2} k_{n2}}{p + \nu_n} \right] S_{n0} \quad (4.1)$$

Where, γ_a is given by,

$$\gamma_a = \frac{R_{a1} p^2 + \gamma_{a1} p + \gamma_{a2}^2}{p + \nu_a}$$

Denoting the term in the square bracket on the left hand side by $G(p)$, equation (4.1) is represented as,

$$\frac{1}{G(p)} \bar{C}_a = R_{a1} C_{a0} + \frac{\omega R_{n1}}{\gamma_n + \omega} C_{n0} + \frac{R_{a2} k_{a2}}{p + \nu_a} S_{a0} + \left[\frac{\omega}{\gamma_n + \omega} \right] \left[\frac{R_{n2} k_{n2}}{p + \nu_n} \right] \quad (4.2)$$

For two domain models, R_{n1} is not equal to zero. The function $G(p)$ in its most general form is expressed as a ratio of two polynomials as given.

$$G(p) = \frac{b_3 p^3 + b_2 p^2 + b_1 p + b_0}{a_4 p^4 + a_3 p^3 + a_2 p^2 + a_1 p + a_0} \quad (4.3)$$

For single domain models, R_{n1} is zero. Then the function $G(p)$ is given by,

$$G(p) = \frac{1}{\gamma_a} = \frac{p + \nu_a}{R_{a1} p^2 + \gamma_{a1} p + \gamma_{a2}^2}$$

Where,

$$b_3 = R_{n1}$$

$$b_2 = \gamma_{n1} + \omega + R_{n1} \nu_a$$

$$b_1 = \gamma_{n2}^2 + \gamma_{n1} \nu_a + \omega \nu_n$$

$$b_0 = \gamma_{n2}^2 \nu_a + \omega \nu_a \nu_n$$

$$a_4 = R_{a1} R_{n1}$$

$$a_3 = \gamma_{a1} R_{n1} + \gamma_{n1} R_{a1} + \omega R_{a1} + \omega R_{n1}$$

$$a_2 = R_{n1} \gamma_{a2}^2 + R_{a1} \gamma_{n2}^2 + \omega \gamma_{n1} + \omega \gamma_{a1} + \omega R_{n1} \nu_a + \omega R_{a1} \nu_n + \gamma_{a1} \gamma_{n1}$$

$$a_1 = \gamma_{n1} \gamma_{a2}^2 + \gamma_{a1} \gamma_{n2}^2 + \omega \gamma_{a2}^2 + \omega \gamma_{n2}^2 + \omega \gamma_{a1} \nu_n + \omega \gamma_{n1} \nu_a$$

$$a_0 = \gamma_{a2}^2 \gamma_{n2}^2 + \omega \gamma_{n2}^2 \nu_a + \omega \gamma_{a2}^2 \nu_n$$

Now, $G(p)$ is taken to the right hand side and the coefficients of C_{a0} , C_{n0} , S_{a0} and S_{n0} are multiplied with the same. This results in an expression of the form,

$$\overline{C}_a = G_{ac}(p) C_{a0} + G_{nc}(p) C_{n0} + G_{as}(p) S_{a0} + G_{ns}(p) S_{n0} \quad (4.4)$$

Where, all the G 's are functions of p and are expressed similar to that of $G(p)$. Denominators of each are same as that of $G(p)$. The expressions of numerator differ.

For the most general case, coefficients in the numerator of $G_{ac}(p)$ are given by,

$$\begin{aligned}
b_3 &= R_{a1} R_{n1} \\
b_2 &= R_{a1} \gamma_{n1} + R_{a1} \omega + R_{a1} R_{n1} \upsilon_a \\
b_1 &= R_{a1} \gamma_{n2}^2 + R_{a1} \gamma_{n1} \upsilon_a + R_{a1} \omega \upsilon_n + R_{a1} \omega \upsilon_a \\
b_0 &= R_{a1} \gamma_{n2}^2 \upsilon_a + R_{a1} \omega \upsilon_a \upsilon_n
\end{aligned}$$

The Coefficients in the numerator of $G_{nc}(p)$ are given by,

$$\begin{aligned}
b_2 &= R_{n1} \omega \\
b_1 &= R_{n1} \omega \upsilon_n + R_{n1} \omega \upsilon_a \\
b_0 &= R_{n1} \omega \upsilon_a \upsilon_n
\end{aligned}$$

The coefficients in the numerator of $G_{as}(p)$ are given by,

$$\begin{aligned}
b_2 &= R_{a1} R_{n1} k_{a2} \\
b_1 &= R_{a2} k_{a2} \gamma_{n1} + R_{a2} k_{a2} \omega \\
b_0 &= R_{a2} k_{a2} \gamma_{n2}^2 + R_{a2} k_{a2} \omega \upsilon_n
\end{aligned}$$

Similarly, $G_{ns}(p)$ is given by,

$$\begin{aligned}
b_1 &= R_{n2} k_{n2} \omega \\
b_0 &= R_{n2} k_{n2} \omega \upsilon_a
\end{aligned}$$

After knowing all the coefficients, the equation (4.4) can be solved using simple mathematical methods. The roots of the polynomial in the denominator can be found by standard analytical methods available for solving a biquadratic equation (Abramowitz and Stegun, 1970). After finding all the zeroes in the denominator, $G(p)$ can be expressed as partial fractions.

$$G(p) = \sum_{i=1}^N \frac{P_i}{p + p_i} \quad (4.5)$$

Where, p_i are all real and nonnegative and are the negatives of the zeroes of the denominator, P_i are the coefficients of the partial fractions, and N is the total number of roots, which may vary from one to four depending on the type of the model.

Substituting all the $G(p)$ s in the equation (4.4) in their partial fraction form and inverting in to the original time domain gives a relation, as given below.

$$C_a = \left[\sum_{i=1}^N P_i e^{p_i t} \right] C_{a0} + \left[\sum_{i=1}^N P_i e^{p_i t} \right] C_{n0} + \left[\sum_{i=1}^N P_i e^{p_i t} \right] S_{a0} + \left[\sum_{i=1}^N P_i e^{p_i t} \right] S_{n0} \quad (4.6)$$

The above expression describes the behavior of nondimensional concentration in time domain. The temporal variations can be obtained by substituting the value of time t . The nondimensional concentrations in other regions and phases can be obtained using the equations, (3.5), (3.6) and (3.7). Though, the expression given above for $G(p)$, is the most general one, it changes depending on the type of the model. For various complexity levels, $G(p)$ has been arrived at. They are given in Table (4.1).

Table 4.3 Forms of G(p) for various complexity levels in models

CASE	MODEL	G(P)
1	Single Region, LEA	$1 / (p + a_3)$
2	Single Region, Kinetics	$(p + b_2) / (p^2 + a_3p + a_2)$
3	Double Region, LEA	$(p + b_2) / (p^2 + a_3p + a_2)$
4	Double Region, Kinetics	$(b_3p^3 + b_2p^2 + b_1p + b_0) / (a_4p^4 + a_3p^3 + a_2p^2 + a_1p + a_0)$

4.3 Column Transport Systems

4.3.1 Analytical Solution

For column transport systems of laboratory scale, and in experiments with packed columns, the porous medium can be assumed to be homogeneous. The dispersivity can be taken as constant in space and time. Though, with this assumption, most of the field-scale heterogeneity is not represented, estimations with these simplifications give reasonable results. The reference length L , is taken equal to the length of the column and the reference time T is,

$$T = \frac{L\theta}{q}$$

Using the above assumptions, equation (3.1) is transformed into laplace domain. The resulting expression is,

$$\frac{1}{R_{a1} G(p)} \bar{C}_a = D \frac{\partial^2 \bar{C}_a}{\partial x^2} - \frac{\partial \bar{C}_a}{\partial x} \quad (4.7)$$

In order to solve the above equation, a constant boundary flux condition has been used. Initially, there will be no solute in the column and a pulse of unit concentration, will be introduced for certain time and after that time, incoming concentration will be zero. That means, if t_0 is the duration of the pulse, the boundary condition at the upstream would be,

$$\begin{aligned} C &= 1 \text{ for } 0 \leq t \leq t_0 \\ C &= 0 \text{ for } t > t_0 \end{aligned}$$

This type of boundary condition is called first type boundary condition. The downstream boundary condition is, concentration gradient becomes zero at a large distance. With these conditions, solution of these type of equations is given by Van Genuchten [1980], and is,

$$\bar{C}_a = \frac{1 - e^{-t_0 p}}{p} e^{\left[1 - \sqrt{1 + \frac{4D}{R_{a1} G(p)}}\right] \frac{x}{2D}} \quad (4.8)$$

Analytical inversion of this equation to the time domain is not possible for general cases. It can be inverted analytically for very simple cases of transport only, for example, transport with no rate-limited sorption, dual porosity or degradation. In such cases, $G(p)$ reduces to, $G(p) = 1/p$. Therefore, a numerical inversion method has been used for the purpose and would be explained later in this section.

For column transport systems, break-through curves are generally more useful than the spatial distributions. The temporal moments of the plume at any distance can be obtained using the Aris method, as used by Goltz et. al., [1987] and Valocchi [1990]. In this method, the exponential term in the definition of laplace transform is expanded in the powers of (pt) and are differentiated successively. This results in,

$$M_n^t = (-1)^n \left[\frac{d^n \bar{C}_a}{d p^n} \right]_{p=0} \quad (4.9)$$

Where, M_n^t is the n th absolute temporal moment of C_a .

The quantity of practical significance is the first absolute moment, normalized with mass, which is nothing but the mean arrival time of the break-through curve. Also, the normalized second and third moments taken about the mean arrival time, are needed to estimate physical parameters like dispersion and skewness.

Using (4.9) directly will make the evaluation of the same difficult, as the expression (4.8) involves exponential terms, and also is a ratio. Instead, a slightly modified version of (4.9) will be used, which will directly give normalized first moment and the normalized central second and third moments. It is given as,

$$\mu_n^t = (-1)^n \left[\frac{d^n \ln \bar{C}_a}{d p^n} \right]_{p=0} \quad (4.10)$$

Where, μ_n^t is the n th absolute temporal moment of C_a normalized with mass. The above equation has an advantage that any factor involving exponential is greatly simplified. Also, the transformed solution would involve multiplication of several factors, which can be evaluated separately.

Using this approach, the contributions of various terms in the equation (4.10) towards the mean arrival time, the variance, and the skewness are listed in the table (4.2), given below.

Table 4.4 Contributions of various terms in C_a towards its time domain equivalent

Function	$(1 - \exp(-pt_0))/p$	$\text{Exp}\{-0.5x [\sqrt{(1+4DH(p)/R_{a1})}-1]/D\}$
M_0^t	t_0	$\text{Exp}(-x(H_1-1)/2D)$
μ_1^t	$t_0/2$	$xH'(0)/H_1$
μ_2^t	$t_0^2/12$	$2DxH'(0)^2/H_1^3 - xH''(0)/H_1$
μ_3^t	0	$12D^2xH'(0)^3/H_1^5 - 6DxH'(0)H''(0)/H_1^3 + xH'''(0)/H_1$

Where,

$$H(p) = 1/G(p)$$

$$H_1 = \sqrt{(1 + 4DH(0))}$$

$$H_2 = H_1 (1 + H_1)$$

The expressions for $H(0)$ and its successive derivatives are given as,

$$H(0) = a_0/b_0$$

$$H'(0) = (a_1b_0 - a_0b_1)/b_0^2 \quad (4.11)$$

$$H''(0) = 2(a_0b_1^2 - a_0b_0b_2 + a_2b_0^2 - a_1b_0b_1)/b_0^3$$

$$H'''(0) = 6(2a_0b_0b_1b_2 - a_1b_0^2b_2 - a_0b_1^3 + a_1b_0b_1^2 - a_2b_0^2b_1 + a_3b_0^3 - a_0b_0^2)/b_0^4$$

The above-derived moments can be used to find out the physical quantities like velocity and dispersion coefficient. The effective velocity of the flow is given by,

$$v_{eff}^t = \frac{x}{\mu_1^t} \quad (4.12)$$

According to the fickian model of dispersion, dispersion coefficient can be obtained from the break-through curves. The effective dispersion coefficient can be related to the moments of the break-through curve using the expression,

$$D_{eff}^t = \frac{\mu_2^t}{2 \mu_1^t} (v_{eff}^t)^2 \quad (4.13)$$

4.3.2 Numerical Inversion

4.3.2.1 Introduction to the method

In order to invert the equation (4.8), which is in the laplace domain, in to the original time domain, a numerical technique has been used. Hosono [1981], suggested a method for ILT problems. The essential point of this method is to approximate the exponential term in the definition of ILT by the function, $E_{ac} = \exp(a)/\cosh(a-s)$. This can be expanded in to an infinite series from which an approximate of inverse transform can be obtained.

4.3.2.2 Methodology

The inverse laplace transform is defined as,

$$L^{-1}\{F(s)\} = f(t) = \frac{1}{2\pi j} \int_{\gamma-j\infty}^{\gamma+j\infty} F(s) e^{st} ds \quad (4.14)$$

- Let, 1) $F(s)$ is defined in $\text{Re } s > 0$
- 2) $F(s)$ is regular
- 3) $|s| \rightarrow \infty, F(s) \rightarrow 0$
- 4) $F^*(s) = F(s^*)$, where, $*$ is the complex conjugate.

$$\begin{aligned}
 E_{ac}(s, a) &= e^a / 2 \cosh(a - s) \\
 &= \left[\frac{e^a}{2} \right] \sum_{n=-\infty}^{\infty} j(-1)^n / [s - a - j(n - 0.5)\pi] \\
 &= e^s - e^{-2a} e^{3s} + e^{-4a} e^{5s} - \dots
 \end{aligned} \tag{4.15}$$

The approximated inverse transform is defined as,

$$f_{ec}(t, a) = \frac{1}{2\pi j} \int_{\gamma - j\infty}^{\gamma + j\infty} F(s) E_{ec}(st, a) ds$$

On substituting (4.15) in the above expression, $f_{ec}(t, a)$ becomes,

$$f_{ec}(t, a) = \frac{e^a}{t} [F_1 + F_2 + F_3 + \dots] \tag{4.16}$$

Where,

$$F_n = (-1)^n \text{Im } F \left\{ [a + j(n - 0.5)\pi] / t \right\} \tag{4.17}$$

The expression (4.16) involves an infinite series. In order to truncate the this infinite series, a criterion based on euler transformation has been used, which works under the following conditions.

- 1) There exists an integer $k \geq 1$ so that the signs of F_n alternate for $n \geq k$.
- 2) For $n \geq k$, $\frac{1}{2} < \left| F_{n+1} / F_n \right| \leq 1$

Under these conditions, (4.15) becomes,

$$f_{ec}(t, a) = \frac{e^a}{t} \left[\sum_{n=1}^{k-1} F_n + 2^{-m-1} \sum_{n=0}^m A_{mn} F_{k+n} \right] \quad (4.18)$$

Where, A_{mn} is recursively defined by,

$$A_{mm} = 1 \quad A_{mn-1} = A_{mn} + \binom{m+1}{n} \quad (4.19)$$

Thus, (l, m)th approximation is found by,

$$f_{ec}^{lm}(t, a) = \frac{e^a}{t} \left[\sum_{n=1}^{l-1} F_n + 2^{-m-1} \sum_{n=0}^m A_{mn} F_{l+n} \right] \quad (4.20)$$

This expression can be used to find out an approximation for ILT problems. The author did not mention any criterion for deciding the input parameters l, m and a. These parameters are to be decided after thoroughly testing the procedure for a given problem.

4.3.2.3 Application to the present problem

Using the expressions (4.20), (4.19) and (4.17), a computer routine in C has been developed to find $C_a(t)$ from the expression (4.8). The code, when run, prompts the user for the values of l , m and a and outputs the values of time and C_a . Break-through curves are built using this routine and are used to find normalized first moment and normalized central second and third moments. They are compared with the analytical solutions given in the previous subsection.

As seen in the equation (4.20), the approximate of the inverted value is a function of a . Hence the value of a , should be chosen carefully. The behavior of the function, to be inverted, in the complex domain should be understood thoroughly. As the method does not provide any special primitives for singularities implicitly, all the singularities of the function are to be avoided before applying the method. The author of the method mentioned that when the value of a , is taken to be 3, the relative error is bound by 0.25%. With the functions, whose exact inversions are available, our experimentation with the method gave satisfactory results with m equal to 10. A value of 40 for l would suffice for the purpose. The effect of a on the inverted value and the relative errors are discussed in detail in the next chapter.

Chapter 5

RESULTS AND DISCUSSIONS

5.1 Introduction

This chapter presents the results obtained from the expressions developed. For batch reactor systems, temporal variation of solution phase concentration in the advective region is presented, along with a sensitivity test of the parameters, namely rate constant and mass transfer coefficient. For column transport systems, break-through curves and moments from both break-through curves and analytical expressions developed in the previous chapter, are presented.

5.2 Data used

For the present study, the physical and chemical parameters are so chosen so as to be representative of organic contaminant transport in a sandy aquifer (Roberts et al 1986; Brusseau, 1992). The data is given in table 5.1.

Table 5.5 Data used for the present study

Parameter	Value
f	0.9
ρ	1.81 g/m ³
θ_a	0.29
θ_n	0.04
$F_a = F_n$	0.1
$K_a = K_n$	0.9 cm ³ /g
$k_{a2}^* = k_{n2}^*$	0.3 d ⁻¹
α^*	0.04 d ⁻¹
$\mu_a = \mu_{a1} = \mu_{a2} = \mu_n = \mu_{n1} = \mu_{n2}$	0 d ⁻¹

5.3 Batch Reactor System

The nondimensional solution phase concentration in the advective region of the flow domain can be obtained as a function of time using the expression (4.6). The concentrations in the other region and phases can be obtained using the expressions (3.5), (3.6) and (3.7). The most general case of two regions, nonequilibrium model has been used here. It is assumed that initially the solute exists only in the solution phase and in the advective region and is taken as unity. (i.e., $C_{a0} = 1$). Along with this assumption, the data given in the table 5.1 is used to arrive at the nondimensional C_a at various time values. The rate coefficient k_{a2}^* is then varied by an order of magnitude to perform sensitivity analysis. The resulting plot is given in figure 5.1.

From the figure 5.1, it can be seen that a smaller value of rate constant leads to a slower variation of concentration with time. As the magnitude of the rate constant is increased, the concentration varies rapidly. A similar sensitivity test is carried

out on the mass transfer coefficient α^* also. Due to the very small value of nonadvective region porosity, the effect of α^* on the concentration profile is minimal.

5.4 Column systems

For column systems also, the data used is same as those used for batch reactor problem, which are given in table 5.1. The specific discharge q^* and dispersion coefficient D^* are chosen to be 0.03m/day and 0.003m²/day, respectively. The length of the column is taken as 2.0m. The column is fed with a solute pulse of unit duration. (i.e., $t_0 = 1.0$).

Using the expressions given in table 4.2 and expressions (4.11), the moments of the break-through curve are obtained. Also, the expression (4.8) is inverted in to the original time domain using the methodology explained in the section 4.3.2. By inverting, the concentration versus time plots are build from which the moments are found by numerical integration. The formulae used for the computation are given below.

$$M_0^t = \sum_{i=1}^{n-1} \frac{C_{ai} + C_{ai+1}}{2} \Delta t$$

$$\mu_1^t = \sum_{i=1}^{n-1} \frac{C_{ai} + C_{ai+1}}{2} \Delta t \left[t_i + \frac{\Delta t}{2} \right] / M_0^t$$

$$\mu_2^t = \sum_{i=1}^{n-1} \frac{C_{ai} + C_{ai+1}}{2} \Delta t \left[t_i + \frac{\Delta t}{2} - \mu_1^t \right]^2 / M_0^t$$

$$\mu_3^t = \sum_{i=1}^{n-1} \frac{C_{ai} + C_{ai+1}}{2} \Delta t \left[t_i + \frac{\Delta t}{2} - \mu_1^t \right]^3 / M_0^t$$

At the initial stages of arriving at the results, the moments computed using the above formulae are compared with their analytical counterparts. The relative errors between the analytical solutions and the computed solutions are computed using the error definition,

$$Error = \frac{|Analytical - Computed|}{Analytical} \times 100 \%$$

The error values so computed are used to fix the parameters required for the numerical inversion technique. The errors for various values of parameters l , m and a are listed in the table 5.2. The value of a specific parameter is changed by keeping the other two parameters equal to the values suggested by the author. For subsequent trials, the parameter values obtained so far are used. When the value of l is more than 30, the error is very low. It indicates that for the present problem, the technique has to be used with a minimum l value of 30. By fixing the value of l at 40, m is varied between 10 and 20. For any value of m greater than 10 error did not show any variation. This implies that m can be taken as 10. By keeping l equal to 40 and m equal to 10, a is changed between 2 to 5. The error steadily decreased as the value of a is increased. For a , equal to 4, the percentage error in zeroth moment is zero up to the second decimal. So, for the present problem the values of l , m and a are chosen to be 40, 10 and 4 respectively. For all the subsequent computations these values are used while using the computer routine.

The development of concentration profiles is observed by plotting concentration versus time at various values of x . The time taken to reach the maximum concentration increased with x . The magnitude of maximum concentration decreased

with increasing x . This agrees with the expected behavior of the column system. The plots are given in figures (5.3), (5.4) and (5.5). The break-through curve, for which x is equal to the length of the column L , is shown in the figure (5.6).

The sensitivity tests, similar to the test done for batch reactor problem for the parameters k and α , is performed. The corresponding break-through curves are shown in figures (5.7) and (5.8). The parameter under consideration has been changed by an order while keeping the other parameter same as given in table (5.1). For high values of rate-constant k , which denotes that the reactions are close to equilibrium, break-through curve has very small skewness since the dispersion is very small. The maximum concentration is higher than that for smaller values of k . When the rate-constant is smaller, the break-through curve is more skewed and spanned for longer time. This infers that the reactions are in nonequilibrium. The corresponding temporal moments are given in table (5.3). When the first order mass transfer coefficient α is varied by order, the break-through curves does not vary much. This indicates that α has very little effect on the phenomenon owing to the fact that the porosity value for nonadvective region is small. The corresponding temporal moments of the break-through curves are given in table (5.4). The skewness of the break-through curves for various values of k and α are illustrated in the figures (5.9), (5.10), respectively.

As noted by Goltz and Roberts [1987], in the absence of transformation, the velocity is independent of the rate-constant. The coefficient of skewness decreases with the increase in the magnitude of the rate-constant. The present study matches with these facts. Analytical moments matched with the computed moments with relative error less than 0.01%. This infers that the method for numerical inversion of laplace transform used in this work can be used to get a very good approximation of the ILT.

Expressions developed in the present study are used to check with the field experiments. The field data illustrated by Brusseau et al [1992] is used for the purpose. Figure 5.14 gives the comparison. It can be seen that the results from the present study matches with the field observations very closely.

Table 5.6 Errors with various parameter values for the inversion

l	m	a	Error in μ_1^t	Error in μ_2^t	Error in μ_3^t
10	6	2	0.176	3.811	87.399
20			0.112	1.656	7.093
30			0.110	1.497	3.225
40			0.110	1.471	3.192
40	10	2	0.110	1.461	6.786
	14		0.110	1.461	6.786
	18		0.110	1.461	6.786
40	10	2.5	0.116	0.236	1.286
		3.0	0.087	0.083	0.256
		3.5	0.011	0.042	0.162
		4.0	0.004	0.009	0.980
		4.5	0.001	0.002	0.440
		5.0	0.000	0.002	0.034

Table 5.7 Temporal moments for different values of k

k	Analytical Moments				Computed Moments			
	Zeroth	First	Second	Third	Zeroth	First	Second	Third
0.03	1.000	6.436	14.852	70.880	1.000	6.436	14.852	70.880
0.3	1.000	6.436	2.735	2.365	1.000	6.436	2.735	2.365
3.0	1.000	6.436	1.523	0.965	1.000	6.436	1.524	0.964

Table 5.8 Temporal moments with various values of α

α	Analytical Moments				Computed Moments			
	Zeroth	First	Second	Third	Zeroth	First	Second	Third
0.004	1.000	6.436	5.287	24.774	1.000	6.436	5.287	24.774
0.04	1.000	6.436	2.735	2.365	1.000	6.436	2.635	2.635
0.4	1.000	6.436	2.480	1.871	1.000	6.436	2.480	1.871

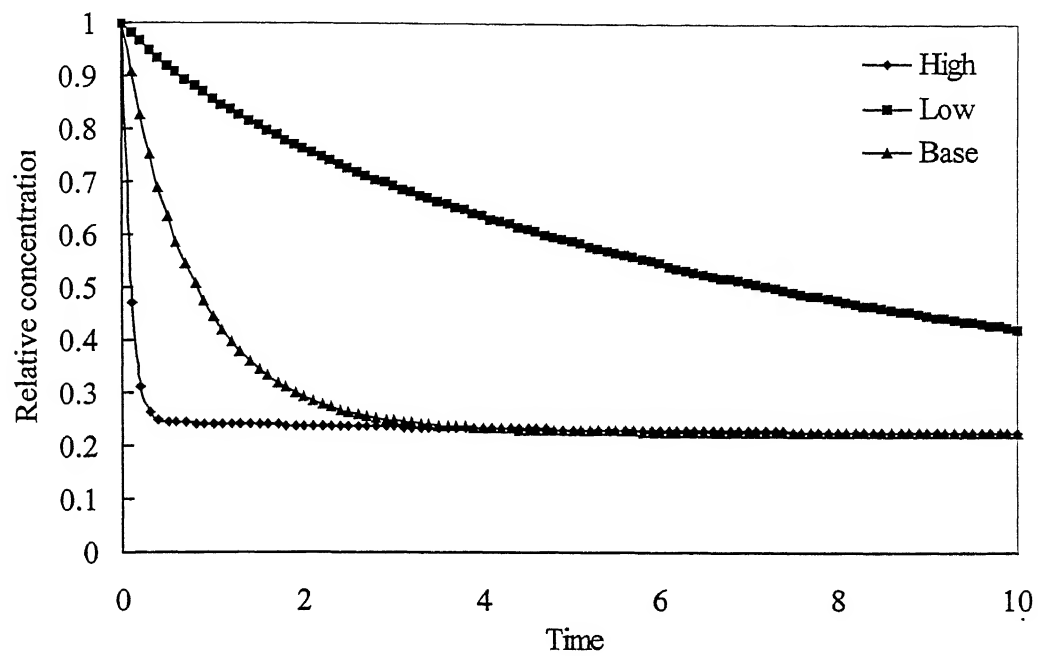


Figure 5.1 Effect of k on concentration

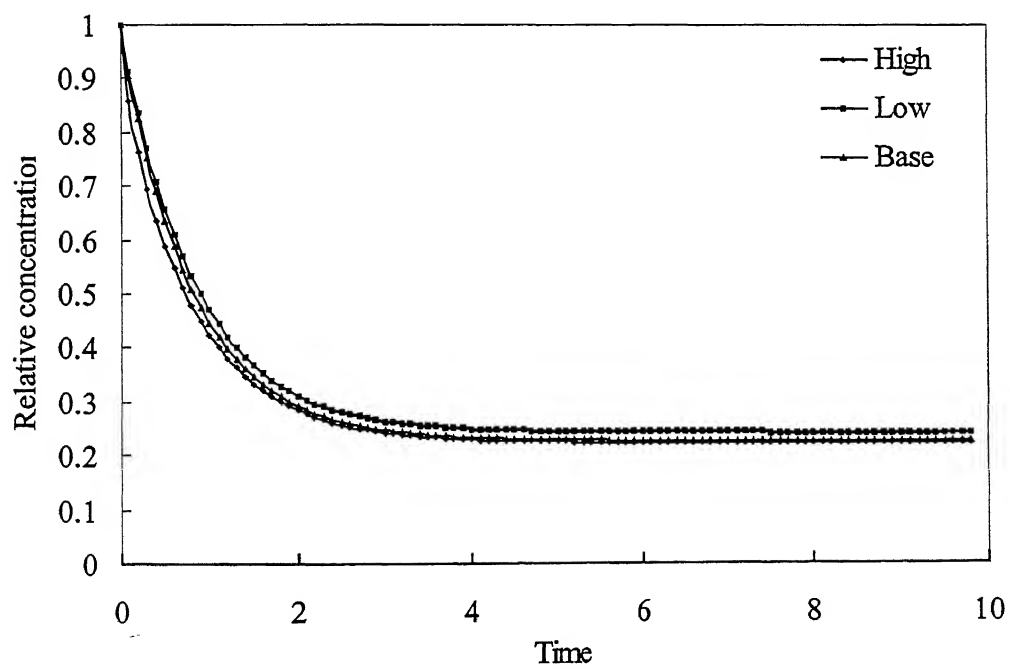


Figure 5.2 Effect of α on concentration

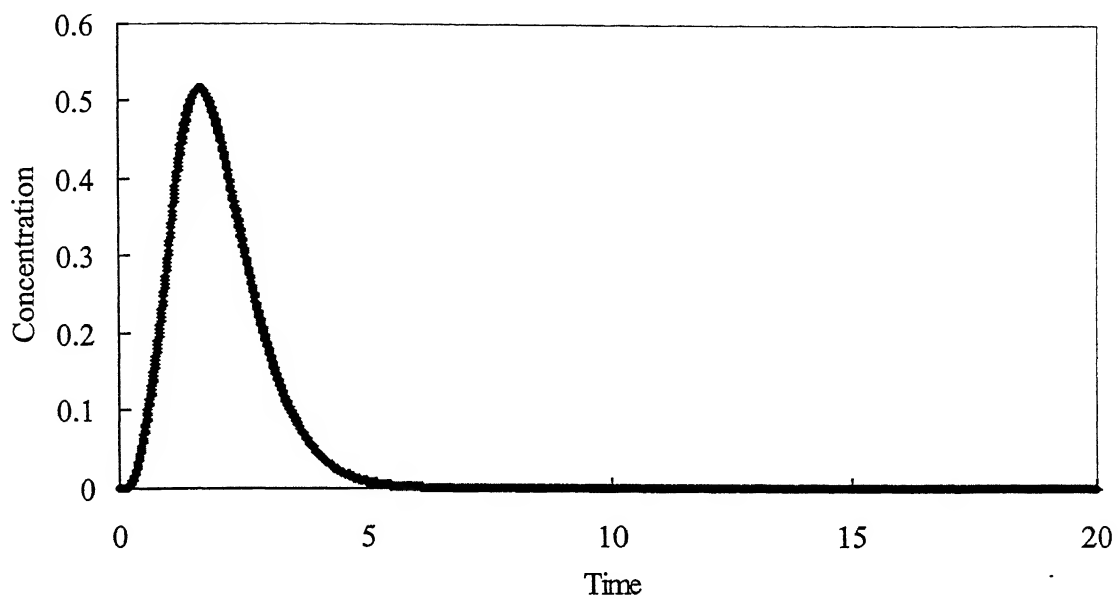


Figure 5.3 Concentration profile at quarter length of the column

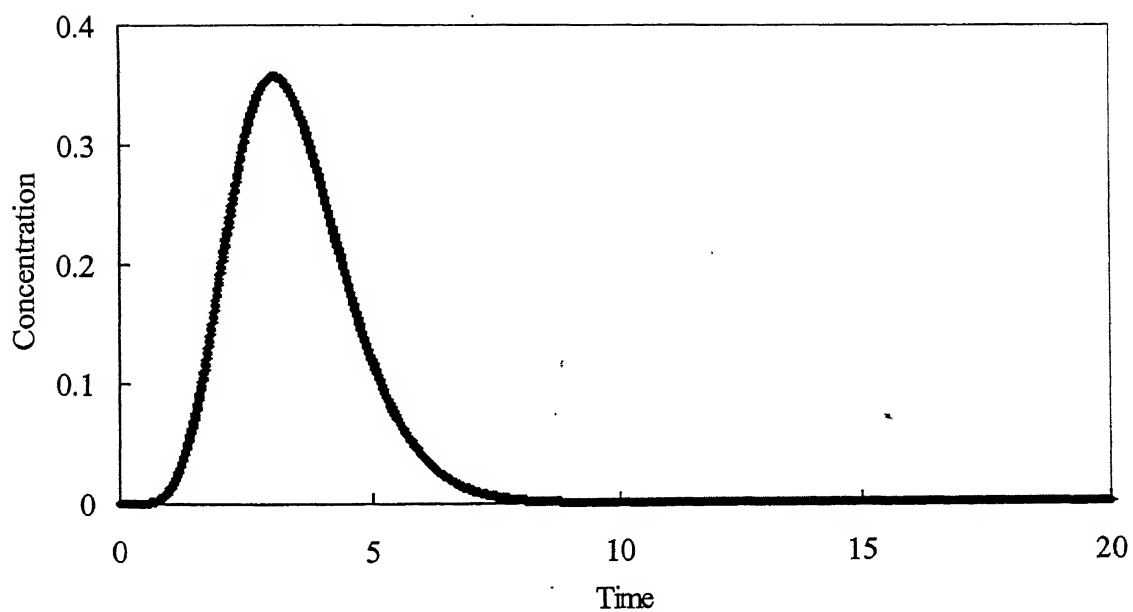


Figure 5.4 Concentration profile at half length of the column

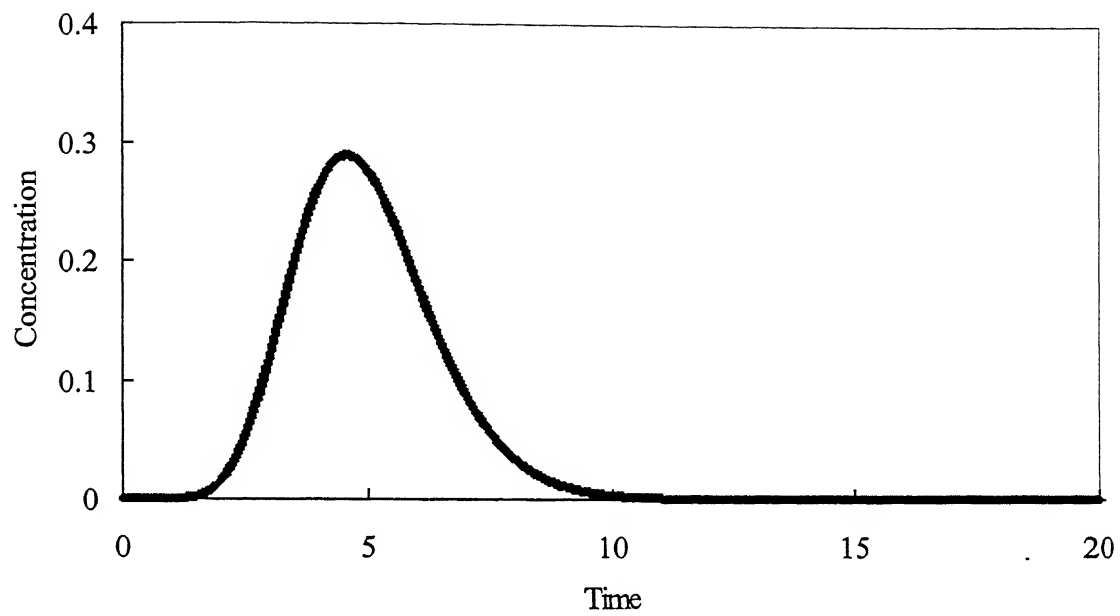


Figure 5.5 Concentration profile at three-fourth length of the column

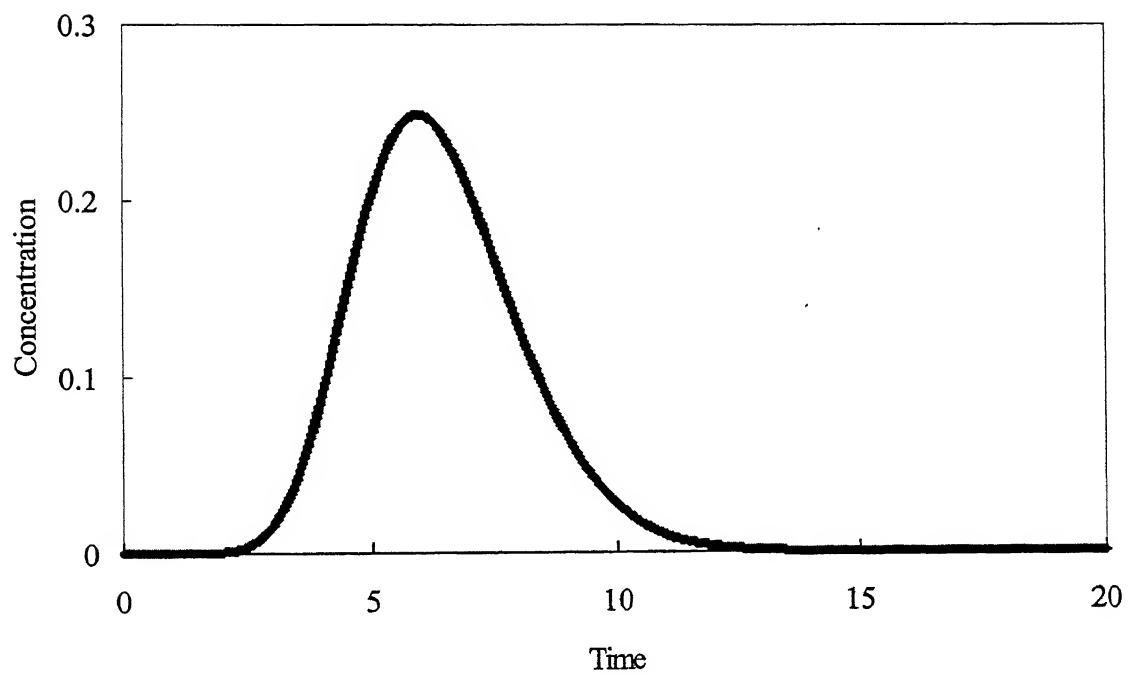


Figure 5.6 The break-through curve

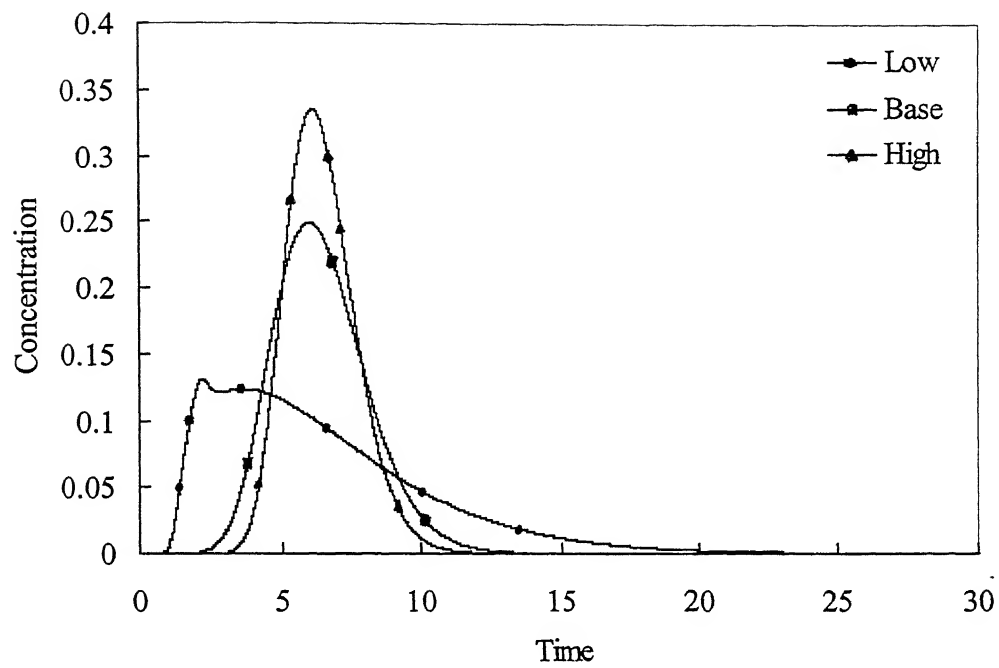


Figure 5.7 Effect of k on break-through curve

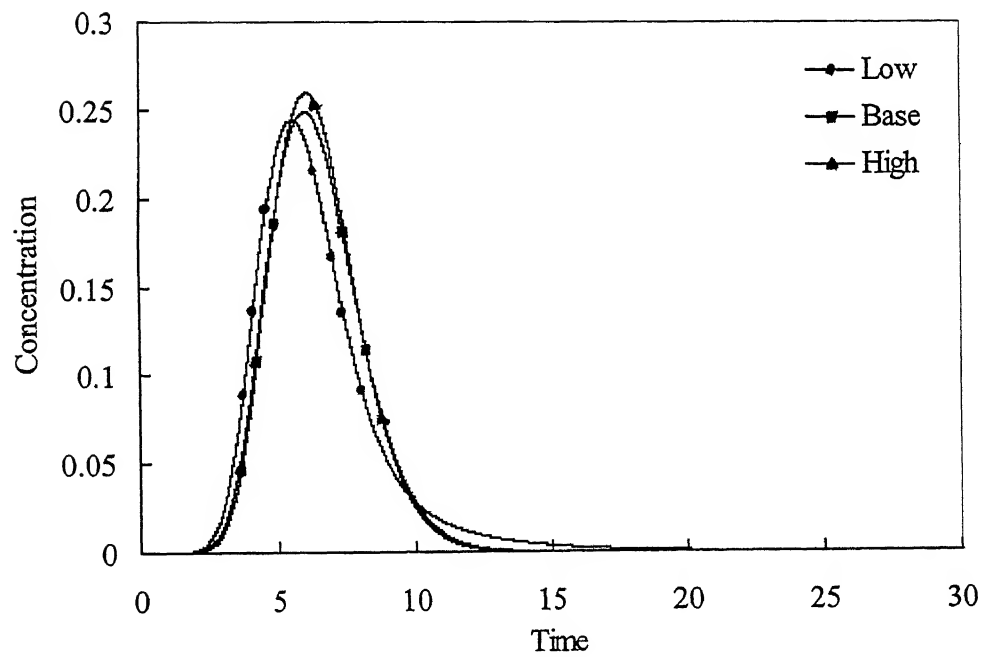


Figure 5.8 Effect of α on break-through curve

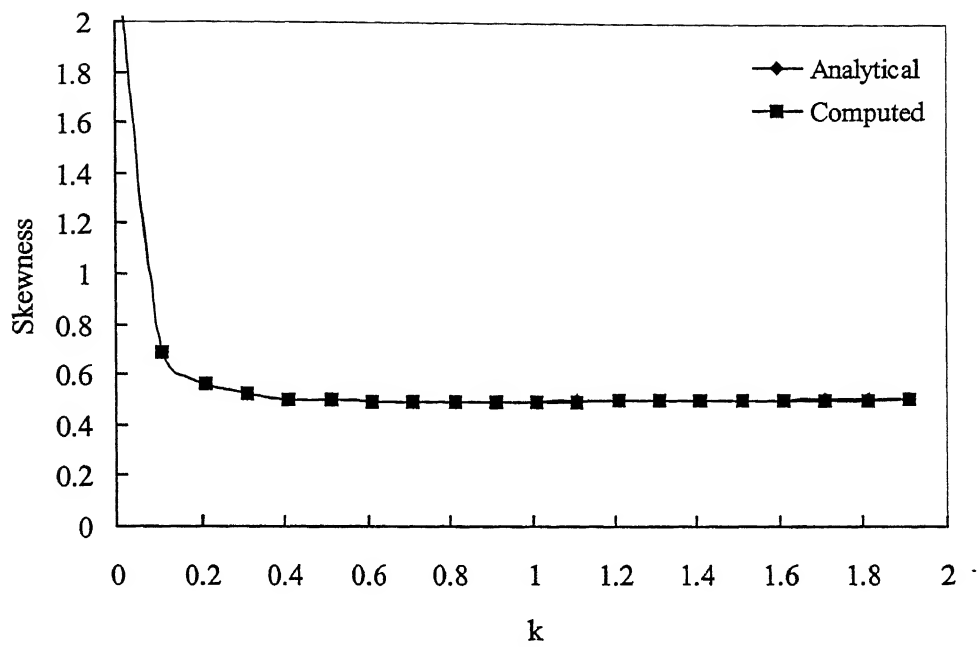


Figure 5.9 Effect of k on skewness of the break-through curve

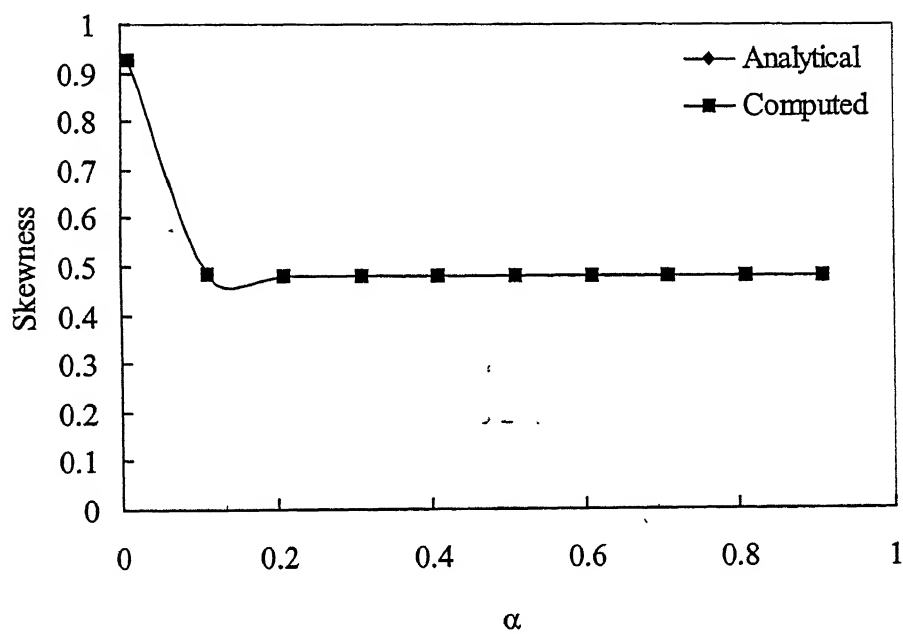


Figure 5.10 Effect α of on the skewness of the break-through curve

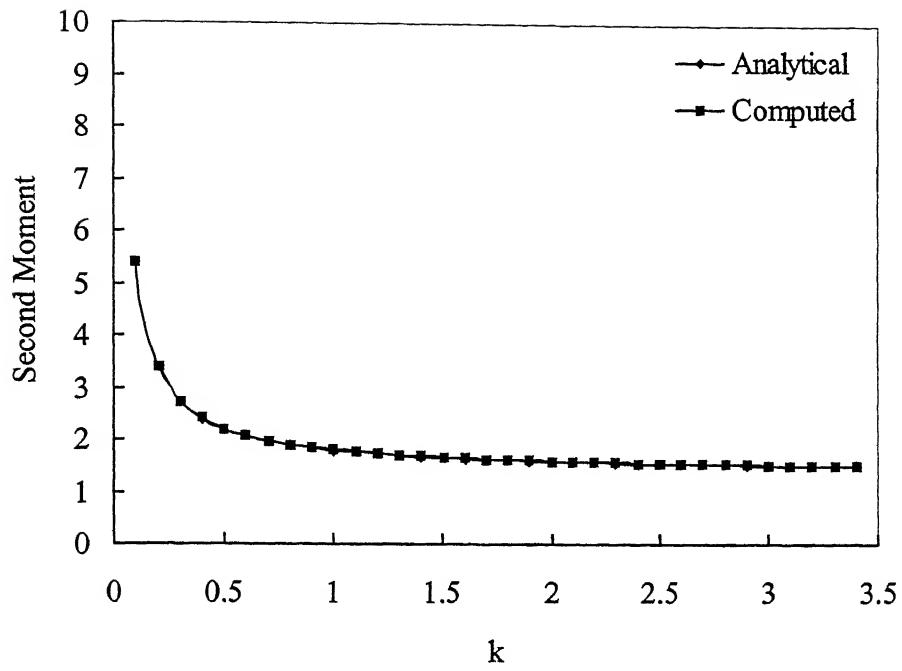


Figure 5.11 Effect of k on second moment

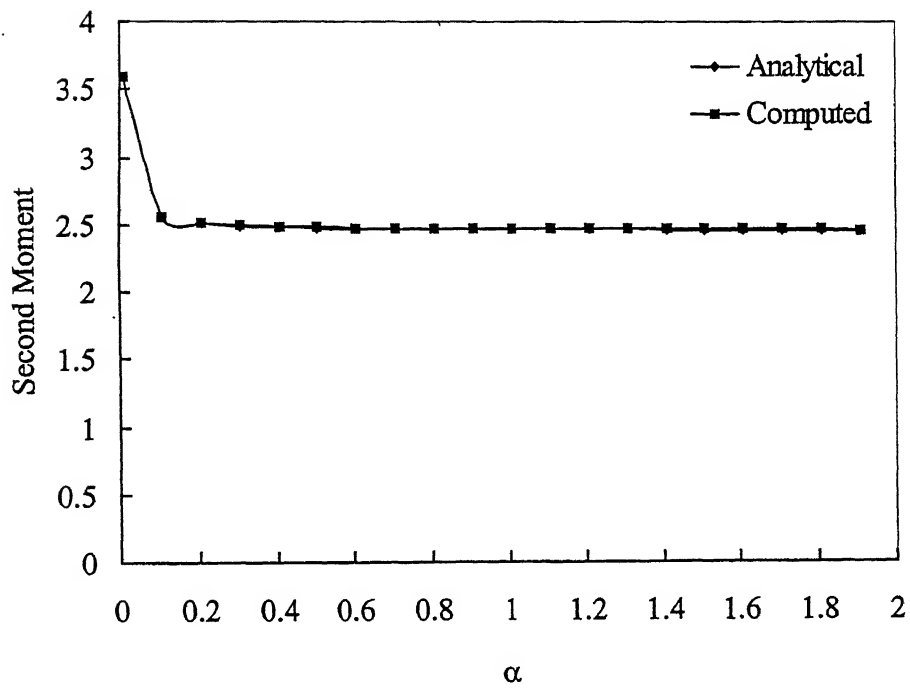


Figure 5.12 Effect of α on second moment

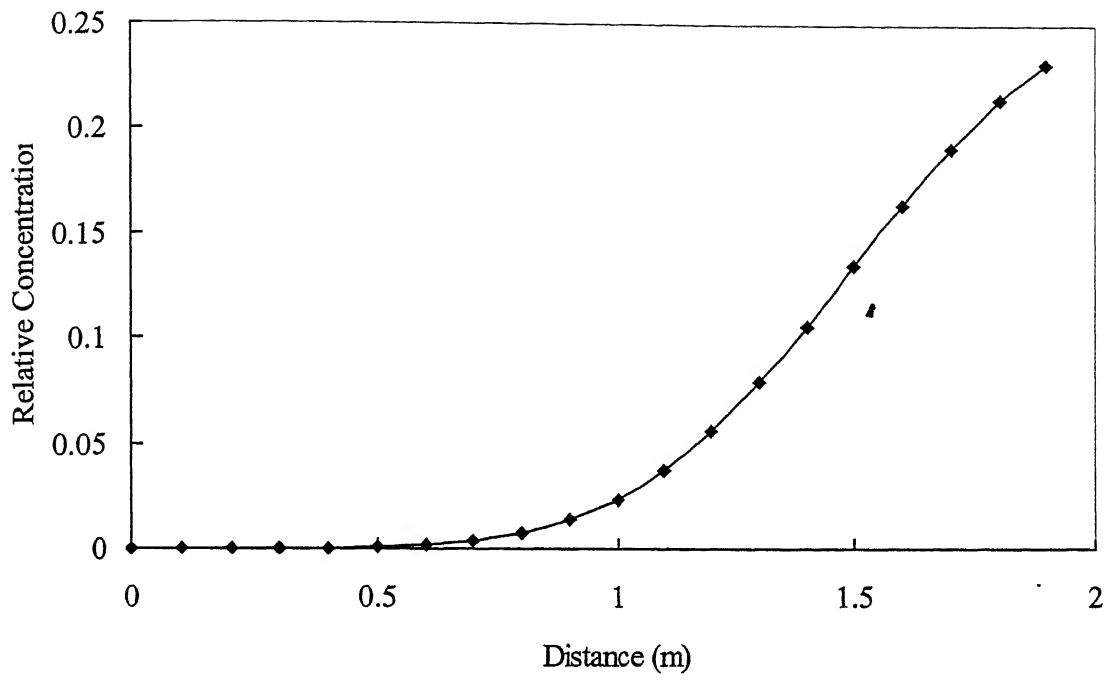


Figure 5.13 Concentration profile at mean arrival time

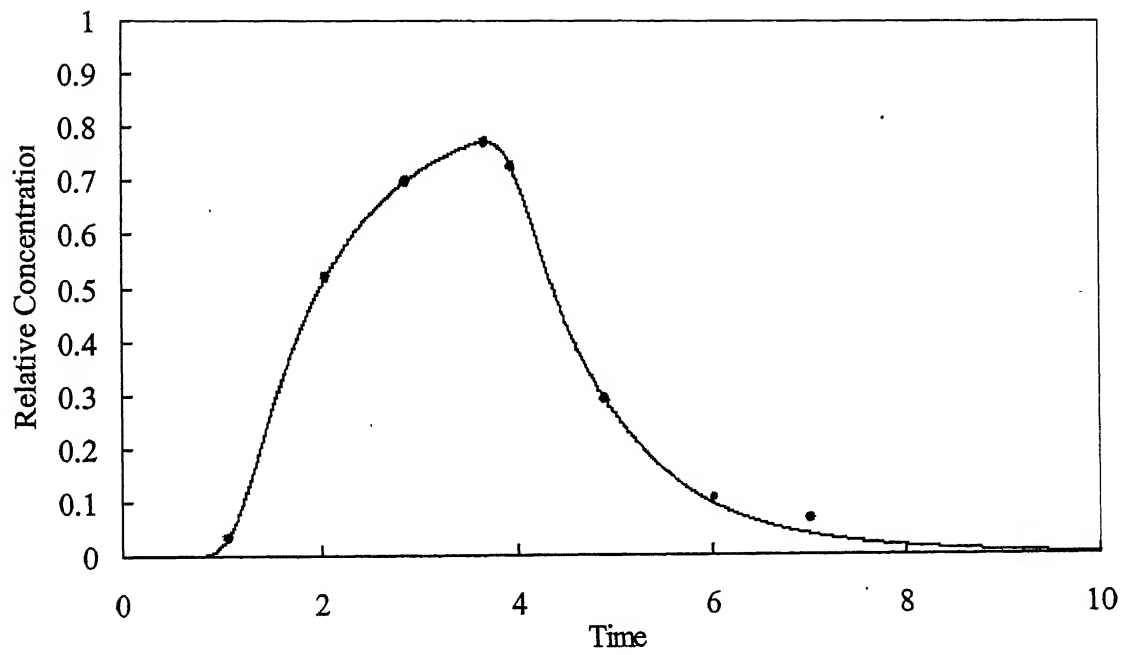


Figure 5.14 Comparison with field observations

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